



United States Environmental Protection Agency
Office of Enforcement and Compliance Assurance
Office of Criminal Enforcement, Forensics and Training

ENFORCEMENT CONFIDENTIAL


NEICVP0973E01

FIELD AND ANALYTICAL REPORT

Western Zirconium, Inc.
Ogden, Utah
NEIC Project No.: VP0973

June 2012

Project Manager:


Richard Ross, Chemist

Other Field Contributors:

John Fowler, Chemist
John Reschl, Chemist
Linda TeKrony, Environmental Engineer

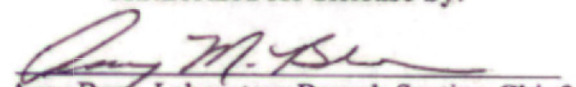
Laboratory Contributing Chemists:

Robert Bohn
James Hoban
Richard Martinez
John Reschl
Jennifer Suggs

Prepared for:

EPA Region 8
1595 Wynkoop Street
Denver, Colorado 80202

Authorized for Release by:


Amy Bern, Laboratory Branch Section Chief

NATIONAL ENFORCEMENT INVESTIGATIONS CENTER
P.O. Box 25227
Building 25, Denver Federal Center
Denver, Colorado 80225-5227

NEIC

CONTENTS

EXECUTIVE SUMMARY	4
SUMMARY OF FINDINGS	4
INTRODUCTION	5
FIELD ACTIVITIES	6
ON-SITE ACTIVITIES	6
Sampling Activities	7
Field Measurements	9
EVIDENCE MANAGEMENT SUMMARY	9
LABORATORY ACTIVITIES	10
INTRODUCTION	10
SUMMARY OF FINDINGS	10
EVIDENCE MANAGEMENT	10
SAMPLE DESCRIPTIONS AND ANALYTICAL APPROACH	10
SUBSAMPLING	12
THERMOMETRY DETERMINATIONS	12
Mason and Cooper Hazard Assessment	17
Thermometry Data Quality Control Measures and Assessment	18
HYDROGEN MEASUREMENTS	19
N.5 Determinations	19
Mason and Cooper Determinations	21
Dumpster Scenario Determinations	22
Ignition Test	23
Hydrogen Gas Data Quality Control Measures and Assessment	23
SULFIDE MEASUREMENTS	24
Acid-Volatile Sulfide Measurements	24
Mason and Cooper Determinations	24
Dumpster Scenario Determinations	25
Hydrogen Sulfide Data Quality Control Measures and Assessment	26
Comparison of Dumpster-Scenario Hydrogen Sulfide Results with Health-Based Limits ..	27
X-RAY FLUORESCENCE RESULTS	29
XRF Data Quality Control Measures and Assessment	30
X-RAY DIFFRACTION RESULTS	30
XRD Data Quality Control Measures and Assessment	31

CONTENTS--continued

TABLES

1	Field Sample Description.....	8
2	Sample Physical Descriptions.....	11
3	Analyses, Analysts, and Methodology.....	11
4	Thermometry Results.....	14
5	Water Volatilized for 10-Gram Tests	17
6	Calculation of Overall Uncertainty for Thermometry	18
7	Thermometry Aliquot Summary Statistics	19
8	N.5 Hydrogen Results.....	21
9	Mason and Cooper Hydrogen Results	22
10	Container Scenario Hydrogen Results	23
11	Acid-Volatile Sulfide Results	24
12	Mason and Cooper Hydrogen Sulfide Results.....	25
13	Dumpster Scenario Hydrogen Sulfide Results	26
14	Hydrogen Sulfide Measurement Bias Assessment	27
15	Dumpster-Scenario Hydrogen Sulfide Average Concentrations for 5, 10-, 15-, and 30-Minute Exposure Durations and Maximum Concentrations, with Statistics.....	27
16	AEGLs for Hydrogen Sulfide	28
17	X-Ray Diffraction Results	31

FIGURES

1	Western Zirconium satellite view, 10000 W 900 S, Ogden, Utah.....	6
2	Crucible cleanout area with grade A material on steel platform	7
3	Apparatus and electronics used for Mason and Cooper testing.....	13
4	Temperature profiles for 10-gram aliquots of samples 30177, 30178, 30179, and 30180... ..	15
5	Temperature profiles for 10-gram aliquots of sample 30178.	15
6	Temperature profiles for 10-gram replicate aliquots of subsample 30178-2.....	16
7	Apparatus used in capturing insoluble reaction gases.	20
8	Hydrogen sulfide headspace profiles for 200-gram sample 30178 triplicate and 200 mL water.....	29
9	Hydrogen sulfide headspace profiles for 200-gram sample 30180 and 200 mL water.	29

APPENDICES

- A NEIC Photographs of Western Zirconium (30 pages)
- B NEIC Infrared Photographs (1 page)
- C NEIC Chain of Custody, Receipt for Samples, and Transfer of Samples Forms (3 pages)

The Contents pages show all of the sections contained in this report
and provides a clear indication of the end of this report.

EXECUTIVE SUMMARY

The U.S. Environmental Protection Agency (EPA) National Enforcement Investigations Center (NEIC) provided field and analytical technical support in an investigation of Western Zirconium, Inc. (Western Zirconium) at the request of EPA Region 8. The field work was completed at Western Zirconium, 10000 W 900 S, Ogden, Utah, on November 8, 2011, and consisted of sampling materials from Western Zirconium's processes.

Samples were subsequently transported to the NEIC laboratory in Denver, Colorado, where they were examined for Resource Conservation and Recovery Act (RCRA) reactivity characteristic properties. All of the samples examined had properties identified under the reactivity characteristic provided in 40 Code of Federal Regulations (CFR) §261.23¹, as is applicable if the material sampled is further classified as a solid waste. All activities of NEIC personnel were performed in accordance with the NEIC quality system.

SUMMARY OF FINDINGS

Upon the addition of water to the materials sampled, considerable heat, hydrogen, and hydrogen sulfide (H₂S) were rapidly generated. Each of these are indicative of properties (2) through (5) found in the reactivity characteristic, 40 CFR §261.23. Detailed findings are provided in the "Field Activities" and "Laboratory Activities" sections of this report.

¹ See 40 CFR §261.23 for the RCRA reactivity characteristic.

INTRODUCTION

NEIC provided field and analytical technical support in an investigation of Western Zirconium at the request of EPA Region 8. Field activities were conducted in November 2011. The facility's website provides that it produces zirconium metal and other products. According to Western Zirconium, it currently receives zirconium as the tetrachloride salt from an off-site source. At the facility, magnesium metal is used to reduce the tetrachloride salt when heated in large crucibles. The molten, reduced product metal forms a layer or "sponge" at the bottom of the crucible, leaving a magnesium chloride top layer that contains impurities. Upon cooling, the magnesium chloride layer forms a cake. A backhoe is used to remove this cake from the crucible. The very top portion of the cake is typically removed first and then discarded at an on-site surface impoundment. It is classified by the facility as the "grade B" material. The remainder of the cake, "grade A" material, is removed, then moved to a hopper where it is conveyed to a comminution device, then sized to minus ¾ inch before it is elevated to an overhead storage silo where it is stored under nitrogen as the product material. Periodically, the silo contents are transferred to rail cars for shipment off-site to the customer.

FIELD ACTIVITIES

ON-SITE ACTIVITIES

On November 8, 2011, an NEIC team (Richard Ross, John Fowler, John Reschl, and Linda TeKrony) conducted sampling and photographed, documented, and conducted field testing of materials at Western Zirconium, Ogden, Utah (Figure 1). Dave Duster (EPA Region 8) accompanied the NEIC team. Photograph logs and photographs documenting site conditions and sample collection are included in **Appendix A**. All field observations and measurements were documented in a bound field logbook. All photographs in **Appendix A** were taken using a Ricoh Caplio 550SE-B camera (serial No. 03301900).



Figure 1. Western Zirconium satellite view, 10000 W 900 S, Ogden, Utah.
Western Zirconium, Inc.
Ogden, Utah

Sampling Activities

Western Zirconium personnel escorted the EPA team to the crucible cleanout area where a crucible containing a layer of magnesium chloride above a layer of zirconium metal sponge was being held for processing. This area is shown in Figure 2.



Figure 2. Crucible cleanout area with grade A material on steel platform
Western Zirconium, Inc.
Ogden, Utah

The crucible was cool and staged for sampling when the NEIC team arrived. For the various grades of magnesium chloride collected for sampling, Western Zirconium personnel were responsible for operating their backhoe and accessing the processed material storage silo. To access the storage silo, Western Zirconium personnel disconnected a transfer line and opened a valve at the base. J. Fowler subsequently collected all samples.

For the sample from Station A, the magnesium chloride grade A, the backhoe was used to remove the solidified material from the top of the crucible. According to company personnel, removable grade B material was not present in this particular crucible. The backhoe operator removed all of the material that he would identify as magnesium chloride grade A. The removed material was spread out into a flat, L-shaped pile around the crucible. The pile was approximately 200 square feet in area and 6 inches deep. A tape measure was used to divide the pile into a grid of fourteen 4- by 4-foot squares. Two of the grid squares were in locations without magnesium chloride due to the L-shape of the pile. The sample increments collected from each grid square were shoveled into plastic 5-gallon buckets lined with doubled plastic liners. A 9- by 11-inch square-point shovel, wrapped in plastic to prevent the metal shovel blade from contaminating the sample material, was used to collect each of the increments. All plastic buckets used for containing samples had internal gap seals integral to their screw caps.

One pile of 14 sample increments was collected on plastic sheeting placed beside the spread-out pile. A second pile of 14 sample increments was collected from approximately the same grid locations as the first set of increments and placed on the plastic sheeting. The entire first pile was shoveled alternately into two 5-gallon buckets using a 6- by 8-inch square-point shovel wrapped in plastic, creating an EPA sample and a split for the facility. Twelve increments were placed into each sample bucket from the first pile. The entire second pile was also shoveled alternately into two 5-gallon buckets, creating an EPA sample and a split for the facility. Thirteen increments were placed into each sample bucket from the second pile. Facility personnel were allowed to select which bucket they wanted for their split sample.

The sample from Station B was collected from a second crucible that contained magnesium chloride grade B, the gray material from the top of the crucible. The backhoe operator removed the material that he would normally classify as magnesium chloride grade B and placed it into a pile under the crucible. A new 9- by 11-inch square-point shovel covered in plastic was used to divide the pile into two sample piles and a discard pile. One increment was shoveled into a 5-gallon bucket, one increment was shoveled into a second 5-gallon bucket (split sample), and eight increments were shoveled into the discard pile. A total of four scoops were shoveled into each sample bucket lined with doubled plastic liners as the pile was sampled.

The sample from Station C was collected from a silo containing crushed magnesium chloride. Facility personnel disconnected a line at the bottom of the silo and opened a valve to allow material to flow out of the silo into a 5-gallon bucket. Three buckets of material were collected from the bottom of the silo and poured onto plastic sheeting, creating a pile. A 5-inch flat-bottom plastic scoop was used to split the entire pile between two 5-gallon plastic buckets lined with doubled plastic liners. Thirteen increments were placed into each 5-gallon bucket, creating an EPA sample and a split for the facility. Table 1 presents the field sample descriptions.

Table 1. FIELD SAMPLE DESCRIPTION
Western Zirconium, Inc.
Ogden, Utah

Station No.	NEIC Sample Tag No.	Sample Collection Date and Time	Station Location	Field Sample Description
A	NE30177 NE30178	11/8/2011 1015 hours	Magnesium chloride grade A	Two 5-gallon buckets, lined with plastic: White flaky solid, with some large chunks
B	NE30179	11/8/2011 1226 hours	Magnesium chloride grade B	One 5-gallon bucket, lined with plastic: Gray flaky solid
C	NE30180	11/8/2011 1119 hours	Crushed magnesium chloride	One 5-gallon bucket, lined with plastic: White flaky material about ½ inch across

Field Measurements

A separate, softball-sized portion of the magnesium chloride grade A was tested on-site to determine if heat would be generated upon wetting. The piece of magnesium chloride grade A was placed on plastic sheeting and moistened with water using a spray bottle. Four pumps of water from the spray bottle were directed onto the upper surface of the magnesium chloride. Each pump delivered approximately 1 gram of water. An infrared camera, FLIR model SC640 (serial No. 309001022) was used to photograph the piece of magnesium chloride before and after it was sprayed with water. The maximum temperature on the surface of the piece of magnesium chloride rose from approximately 78 degrees Fahrenheit (°F) to 223 °F after being wetted. Infrared images of the piece of magnesium chloride are contained in **Appendix B**. "Normal" photographs of this test are located in **Appendix A** (photographs RIMG0018, RIMG0019, RIMG0020, and RIMG0021). R. Ross wet the piece of magnesium chloride with the spray bottle while J. Fowler photographed the reaction with the infrared camera.

Air monitoring using a FirstCheck+1000 multi-gas detector (serial No. 09-1296) was conducted when the sampling team first entered the building where the crucible holding magnesium chloride was stored. This meter was also used to monitor the air about 4 inches above the piece of magnesium chloride as it was sprayed with water. Hydrogen sulfide was detected at 0.1 to 0.2 parts per million (ppm) above the magnesium chloride after it was wetted.

EVIDENCE MANAGEMENT SUMMARY

All samples sent to the NEIC laboratory remained in the custody of NEIC at all times or were secured in a government vehicle. All split samples given to Western Zirconium remained in the custody of NEIC until transferred. Chain of custody, receipt for samples, and transfer of samples forms were prepared by NEIC personnel to document the removal of samples from the site, transfer to Western Zirconium, and transport to the NEIC laboratory. **Appendix C** contains copies of these forms.

NEIC sample tags were prepared and affixed to each sample container by NEIC personnel. The sample containers transported to NEIC were sealed with tamper-evident tape. These samples were placed into the back of the government vehicle and driven to the NEIC laboratory.

LABORATORY ACTIVITIES

INTRODUCTION

40 CFR §261.23 includes the following properties for the RCRA characteristic of reactivity: "(2) It reacts violently with water"; "(3) It forms potentially explosive mixtures with water"; "(4) When mixed with water, it generates toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment"; and "(5) It is a cyanide or sulfide bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment." For the samples received from Western Zirconium, various qualitative and quantitative methods, in conjunction with observations, were used to assess these properties. Several X-ray spectrometry techniques were used to substantiate findings or otherwise assess constituents of the samples collected.

SUMMARY OF FINDINGS

All of the samples collected from Western Zirconium had the reactivity properties provided above, as is applicable if the material is further classified as a solid waste. Upon the addition of water to the samples, considerable heat, hydrogen, and hydrogen sulfide were generated. The techniques and basic criteria used to qualify these findings are provided in the following sections.

EVIDENCE MANAGEMENT

All samples were received by the NEIC Laboratory on November 9, 2011, custody seals intact. Each sample was subsampled into 16-ounce, wide-mouth, glass jars for distribution to various laboratory locations and to preserve the integrity of the samples. The subsamples are designated by the NEIC tag number followed by a sequence number; e.g., 30177-1, 30177-2, 30177-3, etc. For some analyses, the bulk sample or more than one sequenced subsample was used. In such instances, these samples are identified with no sequence number (bulk sample) or with multiple sequence numbers (more than one subsample). The actual sample portions tested are sometimes referred to as "aliquots." All samples were handled in accordance with the NEIC procedure *Evidence Management*, NEICPROC/00-059R3.

SAMPLE DESCRIPTIONS AND ANALYTICAL APPROACH

The physical descriptions of the four samples are summarized in Table 2, along with the assigned sample number and NEIC tag number.

ENFORCEMENT CONFIDENTIAL

Table 2. SAMPLE PHYSICAL DESCRIPTIONS
Western Zirconium, Inc.
Ogden, Utah

NEIC Tag No. Laboratory Sample Designation	Laboratory Physical Description
NE30177 (30177)	Colorless to light-gray layered crystal. Cleaved layers typically pliable. Some hard non-layered more crystalline pieces less than one inch across in at least one dimension.
NE30178 (30178)	Similar to sample 30177
NE30179 (30179)	Similar to samples 30177 and 30178; however, typically more gray in color and somewhat higher proportion of hard crystalline material.
NE30180 (30180)	Similar to samples 30177 and 30178, only with slightly more grayish cast

Table 3 summarizes the analyses performed, the analysts, and the methodology. All analyses were conducted between late December 2011 and April 2012 by NEIC personnel in accordance with the NEIC quality system. The Mason and Cooper testing, the N.5 testing, and container testing described later in this report are not within the scope of NEIC's accreditation.²

Table 3. ANALYSES, ANALYSTS, AND METHODOLOGY
Western Zirconium, Inc.
Ogden, Utah

Parameter/Analysis	Analyst(s)	Methodology
Physical description	Richard Ross	<i>Physical Description/Phase Separation</i> , NEICPROC/00-045R2
Thermometry	John Reschl	Mason and Cooper ¹ ; continuous recording thermocouple/computer interfaced, data acquisition system
Hydrogen	Robert Bohn James Hoban Richard Ross	Volumetric hydrogen measurement, UN N.5 ² or reaction with water into headspace; analysis by gas chromatography ³
Sulfide	John Reschl	Evolution of H ₂ S at pH <2/NaOH trap, or neutral water reaction; followed by gas diffusion/pulsed amperometric detection ⁴
X-ray diffraction (XRD)	Richard Martinez	<i>X-Ray Diffraction for Qualitative Identification of Crystalline Phases</i> , NEICPROC/99-019R2
X-ray fluorescence (XRF)	Jennifer Suggs	<i>X-Ray Fluorescence Spectrometry (XRF) Using the Rigaku ZSX 101e</i> , NEICPROC/02-003R2

¹ Mason, C.M; Cooper, J.C., *Classification of Hazards of Materials – Water Reactive Materials and Organic Peroxides*, Report No. TSA-20-72-2, Department of Transportation, Office of Hazardous Materials, Washington, D.C. NTIS Number PB-209 422, March 1972.

² Test N.5 is taken from the "Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria," 4th Rev. Ed., United Nations, 2003. Although the testing in this report is referred to as N.5, the United Nations method N.5 as given was used only as guidance.

³ ASTM D2504-88 Standard Test Method for Noncondensable Gases in C₂ and Lighter Hydrocarbon Products by Gas Chromatography/ Hewlett-Packard Application Note 228-125/*Analysis of Permanent Gases and Methane with the Agilent 6820 Gas Chromatograph*-Agilent Technologies Application Note, February 1999.

⁴ Milosavijevic, E.B.; Solujic, L.; Hendrix, J.L.; Nelson, J.H., "Flow Injection Gas Diffusion Method for Preconcentration and Determination of Trace Sulfide," *Anal. Chem.* 1988, 60: 2791-2796.

² NEIC is accredited to ISO/IEC 17025:2005 for forensic testing by ANSI-ASQ National Accreditation Board/FQS. Some of the analytical work performed here was not within the scope of the competences recognized by this accreditation.

SUBSAMPLING

Each of the four original samples was spread out on a polyolefin sheet, and the pieces were hand-broken or cut with a stainless steel knife to minus 2 inches in size. A flat-bottom scoop approximately 4 inches wide was used to alternately shovel approximately a dozen increments into each subsample jar. Sample 30180 required no further reduction in size because it represented the minus 3/4 inch ("3/4") product material as processed on-site. Some compositional heterogeneity at the test portion sizes was visually evident for the other samples. Further particle size reduction was not employed because it could accelerate reaction with atmospheric moisture and lead to underestimation of the hydrogen or alter the reaction with water; or the exposure to atmospheric moisture could oxidize sulfide, leading to underestimation of sulfide.

For all samples, the material that remained after subsampling was returned to its original inner plastic packing bag, resealed with minimum ambient air entrainment, returned to the plastic packing bag, and then placed into its respective 5-gallon bucket. The lid was tightly resealed.

THERMOMETRY DETERMINATIONS

Thermometry determinations primarily consisted of recording thermometry measurements and observing reactions of the sample material when mixed with water. The thermometry measurement procedure is based on the Mason and Cooper method developed for the U.S. Department of Transportation and mentioned in the RCRA reactivity characteristic background document.³

A thermometric device patterned on the one referenced in the Mason and Cooper method was used. A thermocouple was electrically connected to a laptop computer. The thermometry cell was a glass (Pyrex™) 32-millimeter (mm) by 200-mm test tube encased at the lower portion in an insulation block. The equipment is shown in Figure 3.

³ Background Document – Resource Conservation and Recovery Act Subtitle C – Identification and Listing of Hazardous Waste – 40 CFR § 261.23 – Characteristic of Reactivity, EPA, May 2, 1980.

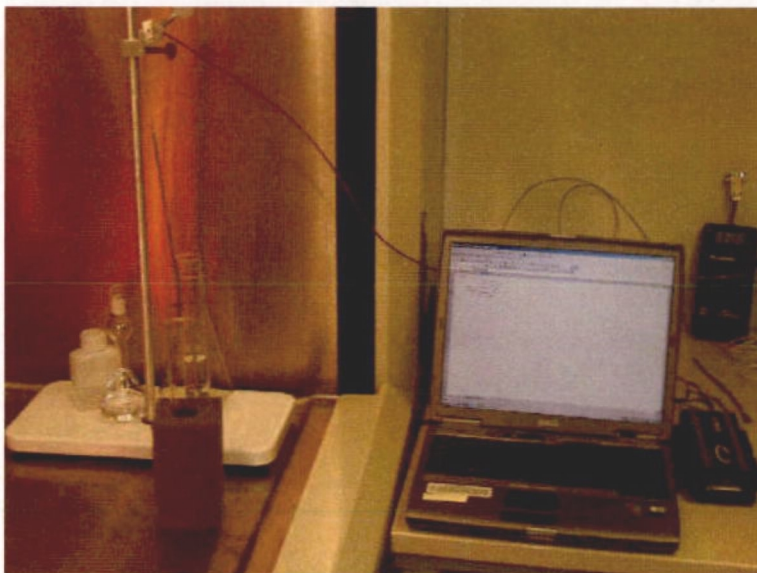


Figure 3. Apparatus and electronics used for Mason and Cooper testing.
Western Zirconium, Inc.
Ogden, Utah

The temperature of the reaction was measured for various masses of sample combined with 10 milliliters (mL) of water. One- and two-gram test portions from all four samples sizzled when water was added. Water condensate formed above the insulation. Dissolution was complete. For the 10- and 20-gram test portions, the water boiled immediately upon the addition of water, steam evolved, and water condensate formed. Undissolved solids were always observed at the end of the determination for the 10- and 20-gram test portions. For the higher-weight test portions, and for a period even after the testing had been completed, the regions near the bottom of test tubes were too hot to hold using bare hands. Upon the addition of rinse water, the water boiled and steam evolved. For a few tests, the smell of rotten eggs was evident. The Mason and Cooper thermometry results are summarized in Table 4.

Table 4. THERMOMETRY RESULTS
Western Zirconium, Inc
Ogden, Utah

Subsample	Test Portion (g)	Tmax °C	ΔT °C	Test Portion (g)	Tmax °C	ΔT °C	Test Portion (g)	Tmax °C	ΔT °C	Test Portion (g)	Tmax °C	ΔT °C
30177-1	1.00	77.58	55.65	2.01	95.56	74.39	10.07	136.31	114.93	20.03	148.25	126.20
30177-2	1.00	81.56	59.65	2.02	98.40	77.20	10.01	135.11	113.74	20.07	141.73	119.66
30177-3	1.01	102.36	80.57	2.00	98.33	77.21	10.02	135.12	113.79	20.01	142.97	120.95
30177-4	1.01	101.53	79.67	2.00	98.06	76.95	10.05	136.48	115.16	20.01	134.55	112.53
30177-5	1.02	66.49	44.66	2.00	99.05	77.91	10.00	140.19	118.71	20.02	141.52	119.57
30178-1	1.03	89.32	67.47	2.02	97.38	76.31	10.03	137.54	115.93	20.00	136.05	113.42
30178-2	1.03	89.90	68.10	2.04	99.68	78.61	10.05	125.33	103.77	20.01	136.79	114.58
30178-3	1.01	72.46	50.67	2.03	98.58	77.46	10.02	130.82	109.42	20.04	136.23	114.15
30178-4	1.04	50.81	28.94	2.05	98.80	77.65	10.03	135.30	113.89	20.08	140.19	118.11
30178-5	1.04	62.28	40.37	2.00	100.02	78.91	10.03	131.33	109.93	20.01	141.03	119.01
30179-1	1.05	53.19	31.38	2.03	100.07	78.86	10.03	127.82	106.77	20.05	137.24	115.40
30179-2	1.01	97.11	75.36	2.04	97.87	76.68	10.01	135.05	114.09	20.00	139.31	117.39
30179-3	1.00	88.08	66.38	2.00	99.42	78.30	10.00	138.68	117.67	20.04	144.27	122.38
30179-4	1.04	64.46	42.74	2.00	99.52	78.37	10.06	134.63	113.51	20.00	139.70	117.81
30179-5	1.05	81.05	59.36	2.02	98.25	77.09	10.01	133.19	112.19	20.03	138.49	116.66
30180-1	1.02	97.64	75.90	2.00	97.68	76.54	10.07	129.54	108.05	20.01	138.94	116.68
30180-2	1.02	94.58	72.87	2.01	100.87	79.72	10.02	133.04	111.52	20.05	139.12	116.77
30180-3	1.00	101.11	79.37	2.01	99.65	78.60	10.06	134.34	112.80	20.01	138.82	116.41
30180-4	1.03	76.08	54.26	2.01	99.95	78.83	10.00	134.50	112.77	20.02	131.46	108.97
30180-5	1.00	90.35	68.47	2.03	99.04	77.87	10.02	133.87	112.23	20.00	137.16	114.64

The temperature profiles shown in Figure 4 illustrate the abrupt temperature rise immediately after water is introduced into the solid phase and thereafter the prolonged decrease in temperature as reactions subside and the system slowly loses heat to the outside environment. All profiles show the intense thermal reaction with water expected for anhydrous magnesium chloride.

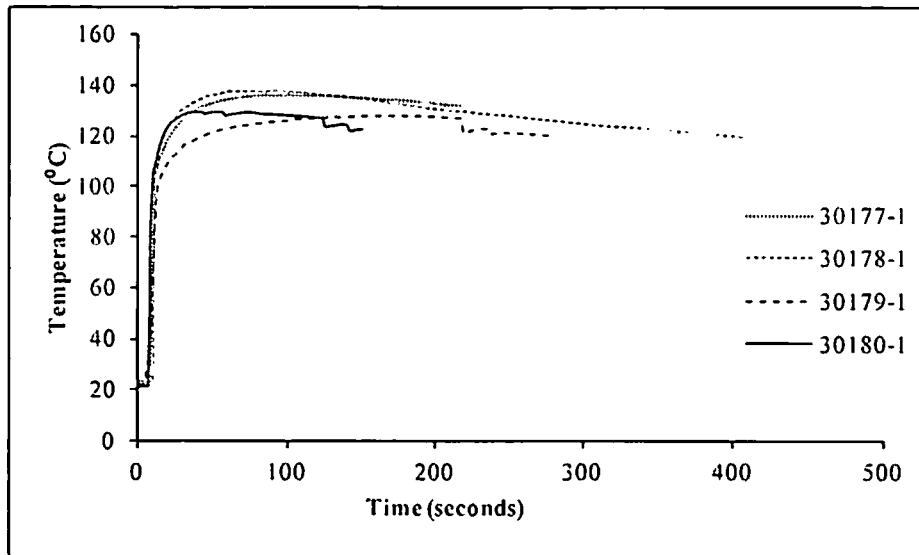


Figure 4. Temperature profiles for 10-gram aliquots of samples 30177, 30178, 30179, and 30180.
Western Zirconium, Inc.
Ogden, Utah

The temperature profiles shown in Figure 4 appear most similar for the aliquots from samples 30177 and 30178. Samples 30177 and 30178 are field duplicates of the grade A material. Sample 30180, representing the product shipped off-site, has a similar temperature profile. For comparison purposes, the range of 130 °C to 140 °C is equal to 266 °F to 284 °F.

The thermometry results for each of the subsamples were very similar. The profiles for the five subsamples from station 30178 illustrate the similarity, as shown in Figure 5.

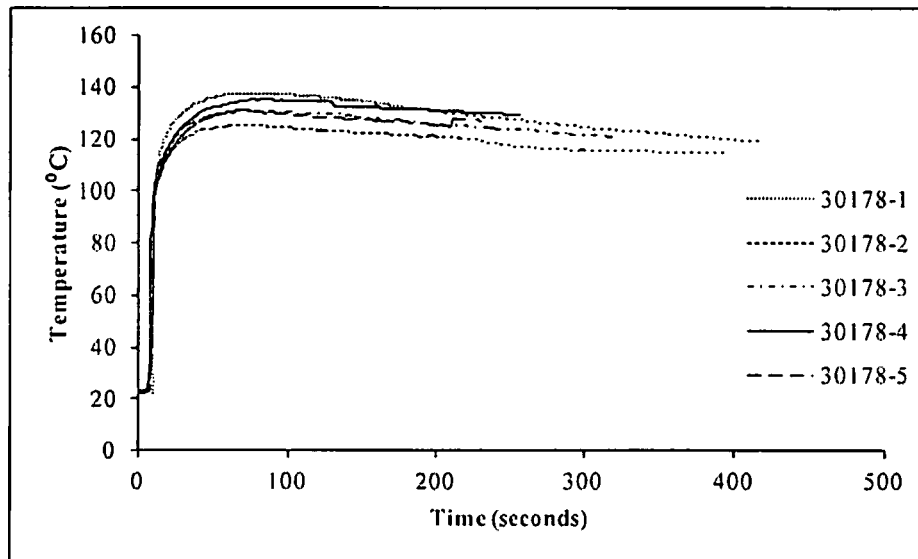


Figure 5. Temperature profiles for 10-gram aliquots of sample 30178.
Western Zirconium, Inc.
Ogden, Utah

The analyst also performed measurements on replicate aliquots within individual subsample jars. Results were very similar, as illustrated in Figure 6, for sample aliquot 30178-2.

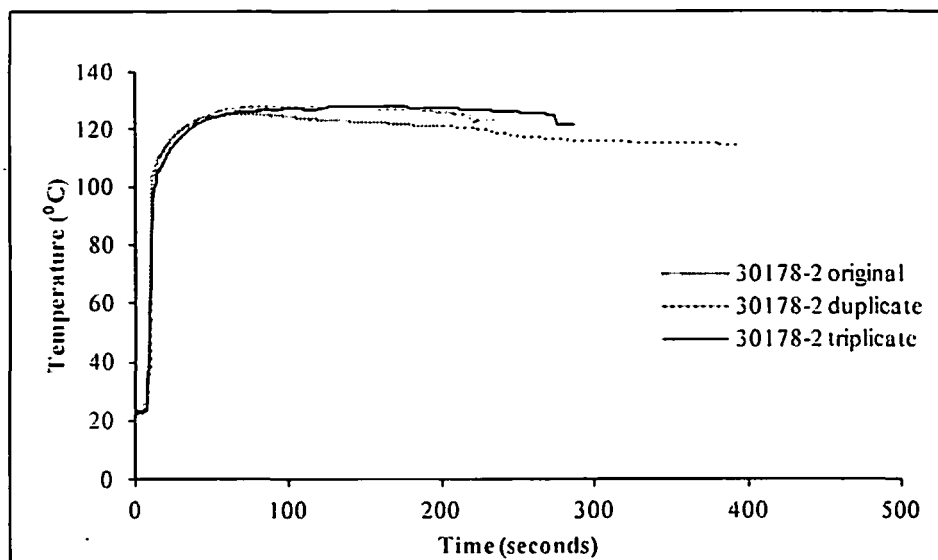


Figure 6. Temperature profiles for 10-gram replicate aliquots of subsample 30178-2.

Western Zirconium, Inc.
Ogden, Utah

For the reaction of 10 mL water and 10-gram aliquots from samples 30177 through 30180, the amount of water volatilized during the reaction was measured gravimetrically. Two measurements were made. The first measurement was the amount of water volatilized and lost from the test tube. The second measurement was the amount of water volatilized and re-condensed on the glass test tube above the insulation. These results and summary statistics are given in Table 5.

Table 5. WATER VOLATILIZED FOR 10-GRAM TESTS
Western Zirconium, Inc.
Ogden, Utah

Subsample	Condensate					
	Aliquot +		Mass	Volatilized	Wipe	
	Aliquot	10mL water			Mass	Volatilized
	grams	grams	Remaining	Mass	Remaining	Mass
30177-4	10.028	19.973	19.426	0.547	18.802	1.171
30178-4	10.056	20.001	19.468	0.533	18.884	1.117
30180-4	10.013	19.958	19.359	0.599	18.916	1.042
30179-4	10.050	19.995	19.365	0.630	18.816	1.179
30179-4	10.010	19.955	19.362	0.593	18.737	1.218
30179-4	10.013	19.958	19.428	0.530	18.817	1.141
			average =	0.584		1.179
			std dev =	0.051		0.039
			%RSD =	8.65		3.26
			std error =	0.029		0.022

Mason and Cooper Hazard Assessment

The Mason and Cooper classifications are provided to rank water reactive materials according to their relative hazard. The order of ranking of the criteria from the most dangerous to least dangerous are:

(3) Danger - Materials which react with water to give temperature rises of 150 °F and evolve toxic or flammable gases.

(2) Warning - Materials which react with water to give temperature rises greater than 150 °F or evolve toxic or flammable gases

(1) Caution – Materials which react with water but give temperature increases less than 150 °F

A temperature rise of 150 °F is equal to 65.56 °C. Temperature rises observed for the 10-gram test portion size were more than 180 °F. As reported in the following sections, hydrogen, a flammable gas, and hydrogen sulfide, a toxic gas, were also evolved in the reactions with water. Because hydrogen and/or hydrogen sulfide are generated by the addition of water, the hazard classification is Danger, Class 3, for these materials. The violent reaction of 20 grams of sample 30177 with water is depicted in **Video 1** (click to view using QuickTime 7 player).

Thermometry Data Quality Control Measures and Assessment

Quality control measures included comparing the thermocouple-determined temperatures to those made with a high-accuracy hand-held thermistor thermometer (HH42), multiple measurements of room temperature and boiling water, and measurements of heats of neutralization. Table 6 provides the method of combining the various measured systematic and random contributions in assessing the combined uncertainty⁴ of the control sample measurements.

Table 6. CALCULATION OF OVERALL UNCERTAINTY FOR THERMOMETRY
Western Zirconium, Inc.
Ogden, Utah

	heat of neutralization T °C	Type K to HH42 T °C	boiling point T °C	HH42 calibration T °C
	0.13	- 0.03	0.45	0.01
	-0.75	- 0.65	- 0.56	0.01
	0.07	0.01	- 0.48	
	0.18	- 0.06	- 0.23	
	0.37	0.03	- 0.49	
	0.30	0.00	- 0.88	
	0.21	0.03	- 0.52	
	0.25			
$\Sigma(\text{bias})^2$	0.95	0.43	2.09	
n	8	7	7	
RMSbias	0.34	0.25	0.55	
u(Cref)				0.02
u(bias)	0.69			
Rw	0.35			
u _c	0.78			

The standard errors for the temperature measurements were propagated with the uncertainty for the controls in computing the expanded⁵ (overall) uncertainty for the sample measurements and these uncertainties along the summary statistics are provided in Table 7.

⁴ Magnusson, B.; Naykki, T.; Hovind, H.; Krysell, *Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories*, Edition 2, Version 1.3, NORDTEST Report TR-537, Approved 2004. <http://www.nordtest.org/register/techn/tlibrary/tec537.pdf>. Where, u (Cref) is the uncertainty given in the calibration reports, u (bias) is the uncertainty component of bias, and R_w is the within-laboratory reproducibility estimated in Table 6.

⁵ For the maximum temperature (T_{max}), the expanded uncertainty (U) is $U = 2(u_c^2 + \text{sn}^{-0.5})^{0.5}$, where u_c is the uncertainty calculated from the various control measures and sn^{-0.5} is the standard error for the sample measurements. For the temperature rise (ΔT), because it is a difference of two measurements, $U = 2(2u_c^2 + \text{sn}^{-0.5})^{0.5}$.

Table 7. THERMOMETRY ALIQUOT SUMMARY STATISTICS
Western Zirconium, Inc.
Ogden, Utah

Sample	Statistic	1gram		2gram		10gram		20gram	
		Tmax °C	ΔT °C	Tmax °C	ΔT °C	Tmax °C	ΔT °C	Tmax °C	ΔT °C
30177	average	85.9	64.0	97.9	76.7	136.6	115.3	141.8	119.8
	std dev	15.7	15.7	1.3	1.4	2.1	2.0	4.9	4.9
	n	5	5	5	5	5	5	5	5
	std error	7.0	7.0	0.6	0.6	0.9	0.9	2.2	2.2
	uncertainty	14.1	14.2	2.0	2.5	2.4	2.9	4.6	4.9
30178	average	73.0	51.1	98.9	77.8	132.1	110.6	138.1	115.9
	std dev	17.0	17.1	1.0	1.0	4.7	4.7	2.4	2.5
	n	5	5	5	5	5	5	5	5
	std error	7.6	7.6	0.5	0.5	2.1	2.1	1.1	1.1
	uncertainty	15.3	15.4	1.8	2.4	4.5	4.7	2.6	3.2
30179	average	76.8	55.0	99.0	77.9	133.9	112.8	139.8	117.9
	std dev	17.8	17.8	0.9	0.9	3.9	4.0	2.7	2.7
	n	5	5	5	5	5	5	5	5
	std error	8.0	8.0	0.4	0.4	1.8	1.8	1.2	1.2
	uncertainty	16.0	16.1	1.8	2.3	3.9	4.2	2.8	3.2
30180	average	92.0	70.2	99.4	78.3	133.1	111.5	137.1	114.7
	std dev	9.7	9.8	1.2	1.2	2.0	2.0	3.3	3.3
	n	5	5	5	5	5	5	5	5
	std error	4.3	4.4	0.5	0.5	0.9	0.9	1.5	1.5
	uncertainty	8.8	9.0	1.9	2.4	2.4	2.8	3.3	3.7

HYDROGEN MEASUREMENTS

Hydrogen measurements were performed to determine the hydrogen generation properties of sampled materials when reacting with water. Three different testing procedures were used to evaluate the samples: (1) the N.5⁶, (2) the Mason and Cooper, and (3) the NEIC-developed dumpster scenario.

N.5 Determinations

For the N.5 determinations, volumetric gas generation measurements were made using a liquid displacement apparatus. Hydrogen was measured in the collected gas. For each of the samples examined, between 63 and 86 grams of sample were introduced into a 500-mL flask filled with water. Samples were introduced using a polyolefin capsule covered at one end with a

⁶ Test N.5, United Nations, as referenced in Table 3.

1-inch square piece of Parafilm® to exclude water. The top of the flask was connected to a water-filled inverted burette. To start, the capsule was agitated or spun in the water-filled flask. This dislodged the Parafilm®, allowing water to enter. As the sample reacted with water and produced gas, water was displaced from inside the attached burette. The insoluble gas transferred to the burette could then be measured from the burette graduations. The apparatus is shown in Figure 7.

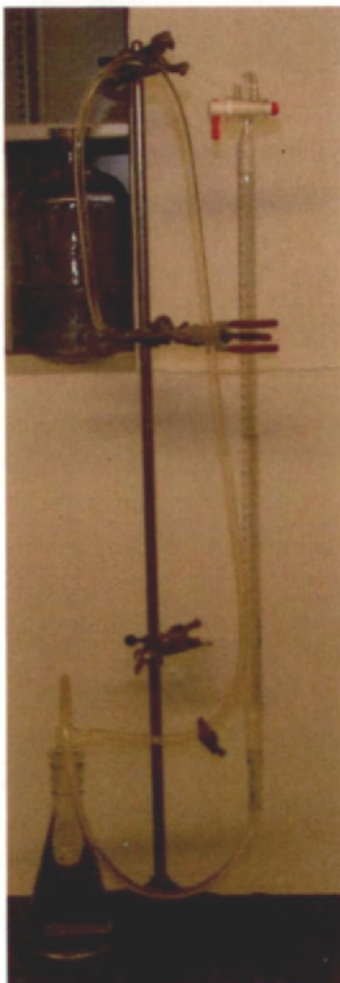
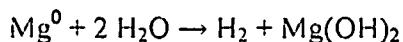


Figure 7. Apparatus used in capturing insoluble reaction gases.
Western Zirconium, Inc.
Ogden, Utah

Ambient pressure was measured with a calibrated aneroid barometer. The final pressure of the gas in the burette was used to correct volumes to standard reference conditions (SRC) (760 torr at 20 °C). The gas produced was exchanged into a small Tedlar® bag from which gas could be sampled using a gas-tight syringe. The duration of the gas formation determinations ranged from approximately 10 minutes to overnight. Hydrogen concentrations were measured using a gas chromatograph equipped with a thermal conductivity detector.

The reaction of elemental magnesium (Mg^0) with water can be considered as follows:



Results are reported according to the free magnesium equivalent of the hydrogen produced in milligrams of elemental magnesium per kilogram of sample (mg Mg⁰/kg) and also in liters of hydrogen gas per kilogram (liters H₂/kg) of sample, corrected for the dissolved hydrogen calculated using Henry's Law. Table 8 summarizes the volumetric hydrogen results.

Table 8. N.5 HYDROGEN RESULTS
Western Zirconium, Inc.
Ogden, Utah

Sample	Mass (grams)	% H ₂ ¹	mg Mg ⁰ /kg	Liters H ₂ /kg ^{1,2}
30177-1	71.74	48	444	0.44
30177-2	85.64	56	442	0.44
30177-3	76.32	46	358	0.35
30178-1	72.19	36	220	0.22
30178-2	81.48	66	705	0.70
30178-3	84.65	61	580	0.57
30178-4	75.23	50	435	0.43
30178-5	79.87	62	771	0.76
30179-1	77.38	53	539	0.53
30179-3	81.93	52	309	0.31
30179-4	77.63	61	713	0.71
30180-1	63.53	39	372	0.37
30180-4	63.45	38	344	0.34
30180-5	63.77	36	318	0.31

¹ Corrected for H₂ dissolved in system water

² At SRC (20 °C, 760 torr)

As shown in the table, the percentages of hydrogen (% H₂) range from 36 to 66 percent. Although some hydrogen sulfide is expected, the collected gas should be mostly hydrogen (H₂) from the reaction of water with magnesium present in the material tested. Air or nitrogen dissolved in the water and introduced with the sample aliquot is the cause of this variation.

Mason and Cooper Determinations

The Mason and Cooper thermometry cell was used to measure hydrogen concentrations in the air above the mixture of water with sample material. These determinations were made by using a gas-tight syringe to withdraw aliquots from the headspace typically 10 to 15 seconds after the addition of water, and then analyzing for hydrogen by gas chromatography. Replicate determinations were performed for each sample, and the average hydrogen concentrations found are summarized in Table 9.

Table 9. MASON AND COOPER HYDROGEN RESULTS
Western Zirconium, Inc.
Ogden, Utah

Subsample	% H ₂ (v/v)	number of tests	Quantitation
			Limit ¹ % H ₂ (v/v)
30177-4	1.1	3	0.1
30178-4	1.5	2	0.1
30179-4	1.4	2	0.1
30180-4	2.6	2	0.1

¹ The quantitation limit is the lowest standard in the calibration

Dumpster Scenario Determinations

This testing using a container ("paint can") is intended to represent disposal of waste into a dumpster or similar enclosure with limited ventilation that is accessible to humans. To evaluate the gas concentrations produced in a semi-confined environment, a 1-gallon, epoxy-lined steel can (new paint can) was used. A loose-fitting lid (used to avoid pressurization) was fitted with two 1/16-inch-diameter thermocouple ports and two gas-sampling ports.

Test portions of the sampled materials were weighed into the can. Two thermocouples were electrically connected to the same temperature-monitoring setup used for the Mason and Cooper testing to produce continuous records of the headspace and liquid temperatures with time. To initiate the test, approximately 200 grams of water were quickly added to approximately 200 grams of the sample and the lid was loosely placed on top of the can.

At timed intervals, the reaction headspace was sampled using glass, gas-tight syringes. The contents then were analyzed for hydrogen using gas chromatography. Table 10 summarizes the headspace hydrogen concentrations over time for the seven tests.

Table 10. CONTAINER SCENARIO HYDROGEN RESULTS
Western Zirconium, Inc.
Ogden, Utah

NE30177		NE30178		NE30178		NE30178		NE30179		NE30180		NE30180	
Time	H ₂	Time	H ₂	Time	H ₂	Time	H ₂	Time	H ₂	Time	H ₂	Time	H ₂
sec	% v/v	sec	% v/v	sec	% v/v	sec	% v/v	sec	% v/v	sec	% v/v	sec	% v/v
8	<0.1	5	<0.1	6	<0.5	6	<0.1	6	<1	30	9.1 ¹	0	2.8
24	1.2	23	1.3	16	1.1	15	0.1	20	1.1	60	3.2	15	5.9
39	0.8	39	1.6	30	1.0	29	<0.1	37	1.2	90	2.3	31	4.2
85	0.7	54	1.5	39	0.8	41	1.2	49	1.7	120	1.8	56	4.4
107	1.8	96	3.1	57	1.2	68	1.7	72	8.9	150	0.8	90	3.8
128	2.8	129	2.2	75	1.4	89	2.0	90	10.8	180	0.8	120	2.9
149	1.7	159	1.8	91	1.3	107	3.6	120	6.0	210	0.9	160	2.4
169	1.3	179	1.5	110	2.0	125	2.2	150	6.7	274	0.7	180	2.2
192	1.0	210	1.4	128	1.9	147	1.6	180	5.2	290	0.8	240	1.9
223	0.7	245	0.6	152	1.5	168	1.2	210	2.9	420	0.4	300	1.7
360	0.6	420	0.9	300	1.0	315	0.8	390	2.8	510	0.7	480	1.4
803	0.4	790	0.8	705	0.5	707	0.6	900	1.7	965	0.4	900	1.0
1260	0.4	1290	0.6	1126	0.3	1200	0.4	1444	1.3	1800	0.2	1500	0.7
1800	0.3	1800	0.5	1800	0.1			1920	1.0			2050	0.5

¹ Exceeded calibration range; estimated concentration.

The potential to create a hazardous atmosphere is evaluated against the lower explosive limit of 4 percent for hydrogen.⁷ Samples NE30179 and NE30180 demonstrated the capability to exceed this threshold.

Ignition Test

An ignition test was attempted. It consisted of adding water to a portion of sample 30177 in a flask with an electronic igniter suspended in the head space. No ignition was observed, which is attributed to the majority of the gas and vapor venting from the system at the elevated temperature created by the violent exothermic reaction of the sample material with water.

Hydrogen Gas Data Quality Control Measures and Assessment

Quantitative analyses included common quality control measures to aid in the assessment of method performance and to ensure data quality. The quantitation limits reported in Table 9 and Table 10 were calculated from the concentration of the lowest calibration standard and sample dilution factors. Hydrogen was not identified in the laboratory air blanks or nitrogen blanks at levels exceeding the quantitation limit (0.1 percent). Known additions of elemental magnesium for the container test resulted in increased headspace hydrogen concentrations.

⁷ Lide, D.R. ed.; Frederikse, H.P.R. ed., *CRC Handbook of Chemistry and Physics*, 77th edition, 1996. CRC Press, New York.

The estimated instrument analytical measurement uncertainty for the hydrogen analysis is based on an evaluation of the 20 quality control check standards (9.98 percent hydrogen), plus 37 daily calibration standards. The mean of the recovery was 94 percent with a relative standard deviation (RSD) of 2.76 percent for 57 standards. The Mason/Cooper test analytical triplicates of sample 30177-4 yielded an RSD of 24 percent. For the N.5 determinations, five analytical replicates of sample 30178 yielded an RSD of 23 percent.

SULFIDE MEASUREMENTS

Sulfide measurements were performed on the sampled materials both to assess the presence of sulfide (S^{2-}) and the hydrogen sulfide (H_2S) gas generation characteristics upon the addition of water. Three different testing procedures were used to evaluate the samples: (1) acid-volatile sulfide, (2) Mason and Cooper-derived hydrogen sulfide, and (3) the NEIC-developed dumpster scenario assessing hydrogen sulfide generation over time.

Acid-Volatile Sulfide Measurements

Acid-volatile sulfide was determined by acidifying measured quantities of the samples placed in Conway diffusion cells containing 0.1N sodium-hydroxide-trapping solution. The sulfide was measured by analyzing the resulting trapping solution using flow injection analysis (FIA)/membrane gas diffusion/pulsed amperometry.⁸ The acid-volatile sulfide results are summarized in Table 11.

Table 11. ACID-VOLATILE SULFIDE RESULTS
Western Zirconium, Inc.
Ogden, Utah

Sample	Result mg S^{2-} /kg	Std Error mg S^{2-} /kg
30177	1.52	0.57
30178	0.75	0.70
30179	4.14	0.58
30180	0.41	0.08
Detection Limit	0.02	

Mason and Cooper Determinations

The Mason and Cooper thermometry cell was used to assess hydrogen sulfide concentrations generated to the air above mixtures of water and sample material. A volume of 5 mL sampled near the top of the airspace above the reaction mixture (10-gram sample and 10 mL water) was analyzed. The vapor phase generated from the samples was sampled during the first 60 seconds of the reaction. The sampled gas was bubbled into a 5-mL solution of 0.1N sodium

⁸ Milosavijevic, et. al.

hydroxide. The solutions were analyzed by FIA. From the triplicate gas sample results, the average maximum hydrogen sulfide concentrations measured and associated standard errors are summarized in Table 12. The results are reported in parts per million by volume (ppmv) as H_2S .

Table 12. MASON AND COOPER HYDROGEN SULFIDE RESULTS
Western Zirconium, Inc.
Ogden, Utah

Sample	Result	Std Error
	H_2S , ppmv	H_2S , ppmv
30177	31.	4.8
30178	35.	28.9
30179	53.	26.2
30180	33.	1.4
Detection Limit		3.0

Dumpster Scenario Determinations

The hydrogen sulfide dumpster-scenario determinations were made by weighing 200-gram portions of the solid material into 1-gallon cans and then adding 200 mL of water. A septum port was used for access of the hydrogen sulfide. Syringes were used to withdraw 5 mL of the headspace gas at recorded time intervals via the sampling port. Timed individual headspace samplings began when 200 mL of water was added to the solid. After the gas was collected, 5 mL of 0.1N NaOH was drawn to the 5-mL graduated mark. The syringe was then shaken to react the gas-and-trap solution. Trap solution volumes were determined by weighing the syringes empty and then weighing again after the gas-and-trap solution was collected. After final weighing, trap solutions were dispensed from the syringes into autosampler vials for analysis.

The temperature of the headspace gas was measured every second. Ambient air pressure was measured using a calibrated aneroid barometer and recorded at the time of each test. The reported results for headspace hydrogen sulfide concentrations were corrected for temperature and pressure of the headspace for each measurement. Table 13 provides measured headspace hydrogen sulfide concentrations with elapsed times for each container test. The results are reported in parts per million by volume as hydrogen sulfide. The analytical limit of detection calculated from the standard deviation of blank syringe measurements was 3.6 ppmv hydrogen sulfide.

Table 13. DUMPSTER SCENARIO HYDROGEN SULFIDE RESULTS
Western Zirconium, Inc.
Ogden, Utah

NE30177		NE30178		NE30178		NE30178		NE30179		NE30180		NE30180	
Time	H ₂ S	Time	H ₂ S	Time	H ₂ S	Time	H ₂ S	Time	H ₂ S	Time	H ₂ S	Time	H ₂ S
sec	ppmv	sec	ppmv	sec	ppmv	sec	ppmv	sec	ppmv	sec	ppmv	sec	ppmv
8	0.8*	7	1.8*	6	4.3	6	4.3	6	1.7*	0	87.5	6	185
30	51.0	17	79.2	24	87.8	19	134	20	16.8	30	123	16	236
47	57.0	24	97.1	39	63.0	33	120	30	13.9	60	35.8	44	65.9
67	65.2	33	77.1	56	87.7	50	130	46	17.1	90	19.6	67	29.5
90	50.3	42	71.2	80	88.1	68	138	60	17.7	120	14.0	99	20.7
107	33.4	50	75.4	91	93.3	89	142	90	27.3	150	11.1	120	15.7
128	20.8	60	81.2	110	58.9	107	80.3	120	17.4	180	9.7	153	13.4
149	13.9	69	90.0	128	39.2	125	52.0	150	12.4	210	9.0	180	12.7
169	11.2	77	62.5	153	27.1	147	38.5	180	8.4	240	8.0	240	9.1
192	8.3	85	55.2	180	19.4	168	29.0	210	6.7	270	7.1	300	8.8
223	7.0	94	59.9	240	13.0	210	23.1	243	5.8	300	5.8	360	8.4
240	7.0	104	37.5	300	10.5	240	19.1	270	5.0	330	5.9	420	8.7
300	6.0	114	30.3	360	8.9	300	14.6	300	6.0	360	5.7	480	7.2
360	5.3	123	27.7	420	7.6	360	12.8	330	4.8	390	4.9	540	7.0
420	4.9	150	18.5	480	7.3	420	11.5	360	4.7	420	4.6	600	6.7
480	4.2	180	12.7	540	6.1	480	10.4	390	4.5	480	5.0	900	6.7
540	4.2	300	7.9	600	6.0	540	10.2	422	5.4	540	4.3	1200	5.5
600	3.9	360	7.3	900	4.5	600	9.0	480	4.1	600	4.2	1500	5.0
900	2.5*	420	6.9	1200	3.7	900	7.1	540	4.0	900	3.6	1800	4.3
1200	2.2*	480	5.6	1500	2.6*	1200	5.9	600	3.5*	1200	3.1*		
1500	1.5*	540	4.9	1800	3.3*	1500	5.7	900	4.6	1500	2.1*		
1800	1.7*	600	4.0			1800	4.9	1200	3.2*	1800	2.0*		
		900	3.9					1500	2.7*				
		1200	2.7*					1800	2.5*				
		1500	2.8*										
		1800	1.5*										

* Estimated concentration. MDL equaled 3.6 ppmv.

Hydrogen Sulfide Data Quality Control Measures and Assessment

Prior to hydrogen sulfide sample determinations, three certified hydrogen sulfide gas standards were analyzed to assess bias. Six separate tests were conducted for each gas. The average recovery and standard deviation for each calibrant gas are reported in Table 14.

Table 14. HYDROGEN SULFIDE MEASUREMENT BIAS ASSESSMENT
Western Zirconium, Inc.
Ogden, Utah

ppmv H ₂ S	27.	40.	100.
n	6.	6.	6.
ave % recovery	93.1	99.4	98.7
std dev	3.4	2.3	3.7

Known additions of sulfide were made, and the headspace hydrogen sulfide increased substantially. The container test was replicated for samples 30178 and 30180. Results are shown in Table 15.

Table 15. DUMPSTER-SCENARIO HYDROGEN SULFIDE AVERAGE CONCENTRATIONS FOR 5, 10-, 15-, AND 30-MINUTE EXPOSURE DURATIONS AND MAXIMUM CONCENTRATIONS, WITH STATISTICS
Western Zirconium, Inc.
Ogden, Utah

Sample ID	H ₂ S	H ₂ S	H ₂ S	H ₂ S	H ₂ S
	ppmv max	ppmv 5 min	ppmv 10 min	ppmv 15 min	ppmv 30 min
30177	65.2	23.0	13.9	10.3	6.1
30178 org	97.1	33.0	19.5	13.9	8.3
30178 dup	93.3	38.1	22.9	17.0	10.2
30178 trip	141.6	57.7	34.5	25.7	15.8
average =	110.7	42.9	25.6	18.9	11.4
std dev =	26.8	13.0	7.9	6.1	3.9
%RSD =	24.2	30.4	30.6	32.3	33.8
std err =	15.5	7.5	4.5	3.5	2.2
30179	27.3	11.9	8.2	6.8	5.0
30180 org	123.3	26.6	15.7	11.9	7.3
30180 dup	236.3	37.0	22.4	17.2	11.2
average =	179.8	31.8	19.1	14.5	9.3
std dev =	79.9	7.4	4.7	3.7	2.8
%RSD =	44.5	23.2	24.8	25.7	30.3
std err =	56.5	5.2	3.3	2.6	2.0

Comparison of Dumpster-Scenario Hydrogen Sulfide Results with Health-Based Limits

Various organizations have established or recommended health-base limits for hydrogen sulfide in air. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value – short-term exposure limit (STEL) is 5 ppm hydrogen sulfide for 15

minutes.⁹ The National Institute for Occupational Safety and Health (NIOSH) ceiling recommended exposure limit (REL) for hydrogen sulfide is 10 ppm for 10 minutes, and the NIOSH immediately dangerous to life and health limit for hydrogen sulfide is 100 ppm.¹⁰ Table 16 provides the EPA's acute exposure guidelines (AEGLs) for hydrogen sulfide.¹¹

Table 16. AEGLS FOR HYDROGEN SULFIDE
Western Zirconium, Inc.
Ogden, Utah

	Hydrogen sulfide		7783-06-4	(Interim)	
	10 min	30 min	9/10/02 ppm	60 min	4 hr
AEGL 1	0.75	0.6		0.51	0.36
AEGL 2	41	32		27	20
AEGL 3	76	59		50	37

Seven headspace tests were conducted where hydrogen sulfide was measured; three were performed on sample 30178, two on sample 30180, and one each on samples 30177 and 30179. Peak concentrations above 100 ppmv were recorded for one of the 30178 samples and both 30180 samples tested. The 15-minute average hydrogen sulfide concentrations for samples 30177, 30178, 30179, and 30180 exceeded the ACGIH STEL of 5 ppm. The 10-minute average hydrogen sulfide concentrations for samples 30177, 30178, and 30180 exceeded the NIOSH REL of 10 ppm. The 10-minute and 30-minute average hydrogen sulfide concentrations exceeded the EPA's AEGL-1. No hydrogen sulfide measurements were made beyond 30 minutes. The peak, 5-, 10-, 15-, and 30-minute average hydrogen sulfide concentrations are provided in Table 15.

The maximum temperatures of the headspace for the tests were between 96 °C and 98 °C, and the maximums were reached within the first minute of the tests. The time profiles in Figure 8 and Figure 9 show that the maximum hydrogen sulfide coincided with the maximum temperature.

⁹ *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*, ACGIH®, Cincinnati, OH. 2010.

¹⁰ *NIOSH Pocket Guide to Chemical Hazards*. Department of Health and Human Resources, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. September 2005. <http://www.cdc.gov/niosh/npg/npgd0337.html> Last accessed March 9, 2010.

¹¹ United States Environmental Protection Agency. Acute Exposure Guideline Levels (AEGLs). <http://earth1.epa.gov/oppt/aegl/pubs/results57.htm> Last accessed March 9, 2010.

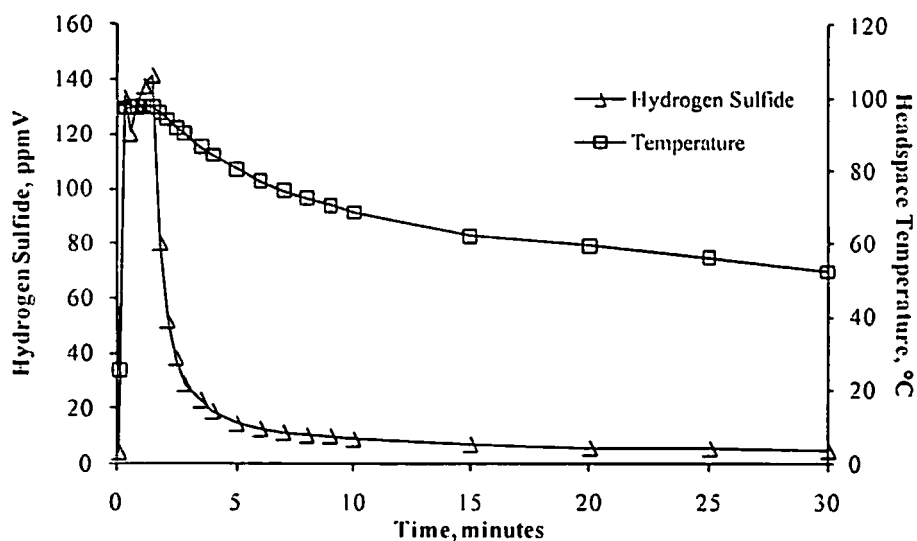


Figure 8. Hydrogen sulfide headspace profiles for 200-gram sample 30178 triplicate and 200 mL water.
Western Zirconium, Inc.
Ogden, Utah

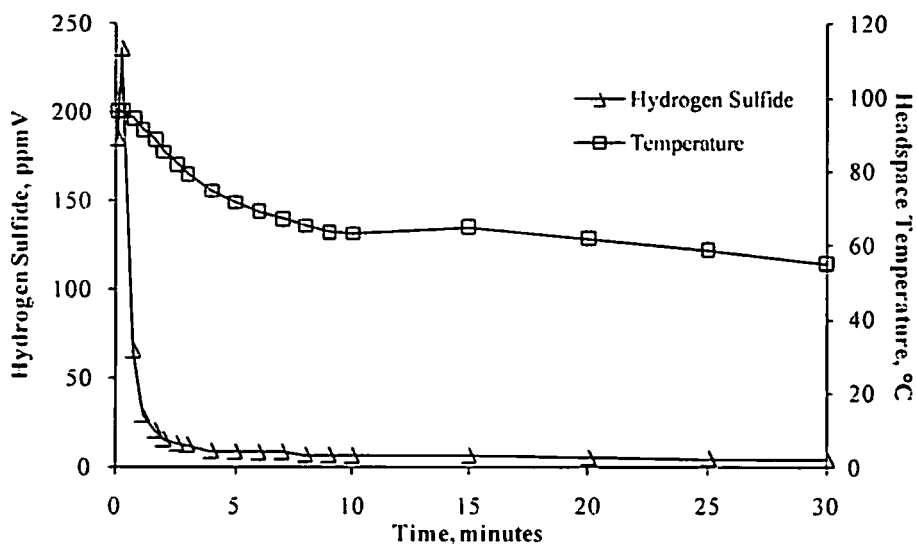


Figure 9. Hydrogen sulfide headspace profiles for 200-gram sample 30180 and 200 mL water.
Western Zirconium, Inc.
Ogden, Utah

X-RAY FLUORESCENCE RESULTS

Aliquots from samples 30177, 30178, 30179, and 30180 were qualitatively analyzed by X-ray fluorescence spectroscopy (XRF).

The samples were prepared using a Spex freezer mill. Samples were then pressed into pellets with boric acid as the side and backing material. Appropriate blanks and other standards

were used as reference materials. A Rigaku fundamental parameters program, EZscan, was utilized in the analysis. The program scans for elements from fluorine (atomic number 9) through uranium (atomic number 92) in the periodic table and identifies the characteristic peaks when present.

The results showed predominating, similar spectra as that for the pure magnesium chloride standard. Zirconium was identified in the approximate range of 0.1 to 5 percent in sample 30178 and in lesser amounts (<0.1 percent) in aliquots of samples 30177, 30179, and 30180. Less than 0.1 percent barium was also identified in samples 30178 and 30179.

XRF Data Quality Control Measures and Assessment

Quality control measures included a boric acid blank pellet, a magnesium chloride pellet, an analytical triplicate pressed from subsample 30178-5, and a standard reference material (SRM), National Institute of Standards and Technology (NIST) 2711. Results from multiple analyses of the NIST 2711 SRM showed reproducibility of measurements for magnesium, zirconium, and barium. Results from the analytical triplicate showed agreement.

X-RAY DIFFRACTION RESULTS

The subsamples 30177-5, 30178-5, 30179-1, 30179-5, 30180-3, and a "nugget" of less than 1 centimeter in diameter from sample 30180 were qualitatively analyzed using X-ray diffraction. The analysis was to identify crystalline phases in the material and offer comparisons to the results found from the other laboratory assessments performed. Portions from each sample were ground with a mortar and pestle for presentation to the instrument. Crystalline phases or compounds are identified by comparing their powder diffraction pattern with reference data from the International Centre for Diffraction Data (ICDD) or with patterns scanned at NEIC from known reference materials. Table 17 summarizes the results for the various samples and standards utilized.

Table 17. X-RAY DIFFRACTION RESULTS
Western Zirconium, Inc.
Ogden, Utah

Significant Compounds Found in Sample/Standard			
Sample/Standard	X'Pert Compound Name other name(s)	Chemical Name	
30177-5	Chloromagnesite	Magnesium chloride	MgCl ₂
30178-5	Chloromagnesite	Magnesium chloride	MgCl ₂
30179-5	Chloromagnesite	Magnesium chloride	MgCl ₂
30179-1	Chloromagnesite	Magnesium chloride	MgCl ₂
30180-3	Chloromagnesite	Magnesium chloride	MgCl ₂
30180 nugget	Chloromagnesite	Magnesium chloride	MgCl ₂
	Bischofite	Magnesium chloride Hydrate	MgCl ₂ ·6H ₂ O
Magnesium chloride standard	Chloromagnesite	Magnesium chloride	MgCl ₂
Silicon standard	Silicon	Silicon - Si	

XRD Data Quality Control Measures and Assessment

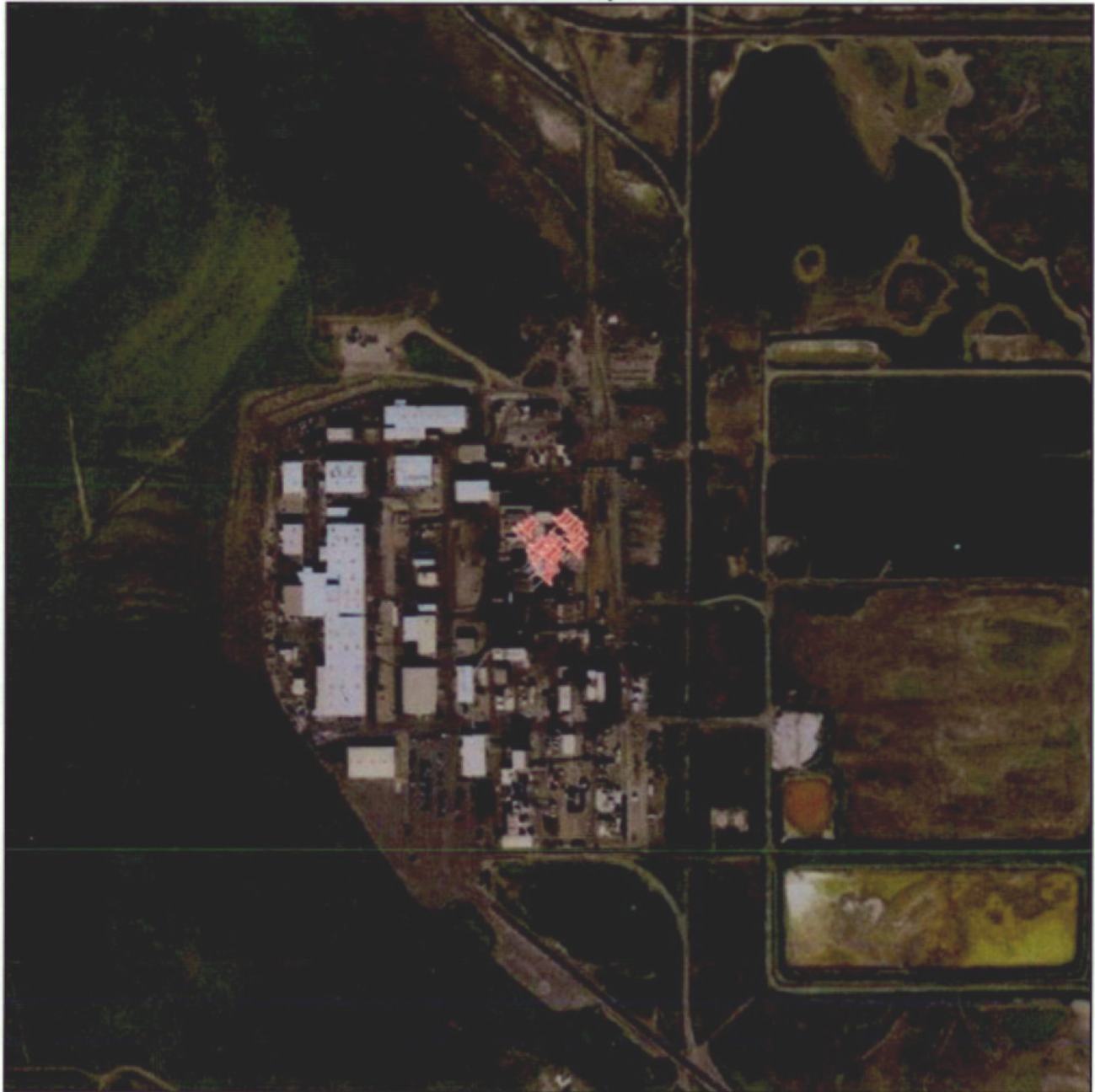
The compounds reported were correctly identified in standards analyzed. A NIST silicon standard was analyzed to verify that the diffractometer was in calibration.

APPENDIX A

NEIC PHOTOGRAPHS OF WESTERN ZIRCONIUM
(30 pages)

Western Zirconium

Overview Map



RIMG0001.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Digout of Crucible
Date Time Stamp	11/8/2011 8:49:46 AM
File Name	RIMG0001.JPG
Latitude	
Longitude	
Photographer	John Fowler

RIMG0002.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Crucible completely dug out with pile of magnesium chloride in front
Date Time Stamp	11/8/2011 9:28:07 AM
File Name	RIMG0002.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0003.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Backhoe spreading out magnesium chloride pile
Date Time Stamp	11/8/2011 9:31:32 AM
File Name	RIMG0003.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 49"
Photographer	Linda TeKrony

RIMG0004.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Spread out pile of magnesium chloride
Date Time Stamp	11/8/2011 9:43:27 AM
File Name	RIMG0004.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0005.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Spread out pile of magnesium chloride
Date Time Stamp	11/8/2011 9:44:16 AM
File Name	RIMG0005.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0006.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Spread out pile of magnesium chloride
Date Time Stamp	11/8/2011 10:02:41 AM
File Name	RIMG0006.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0007.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Piles of magnesium chloride - Two separate samples before splitting (Sample A)
Date Time Stamp	11/8/2011 10:28:50 AM
File Name	RIMG0007.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linde TeKrony

RIMG0008.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Four buckets of split sample (Sample A)
Date Time Stamp	11/8/2011 10:38:03 AM
File Name	RIMG0008.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0009.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Shovel used to spilt sample A
Date Time Stamp	11/8/2011 10:41:26 AM
File Name	RIMG0009.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 49"
Photographer	Linda TeKrony

RIMG0010.JPG
Title: Western Zirconium



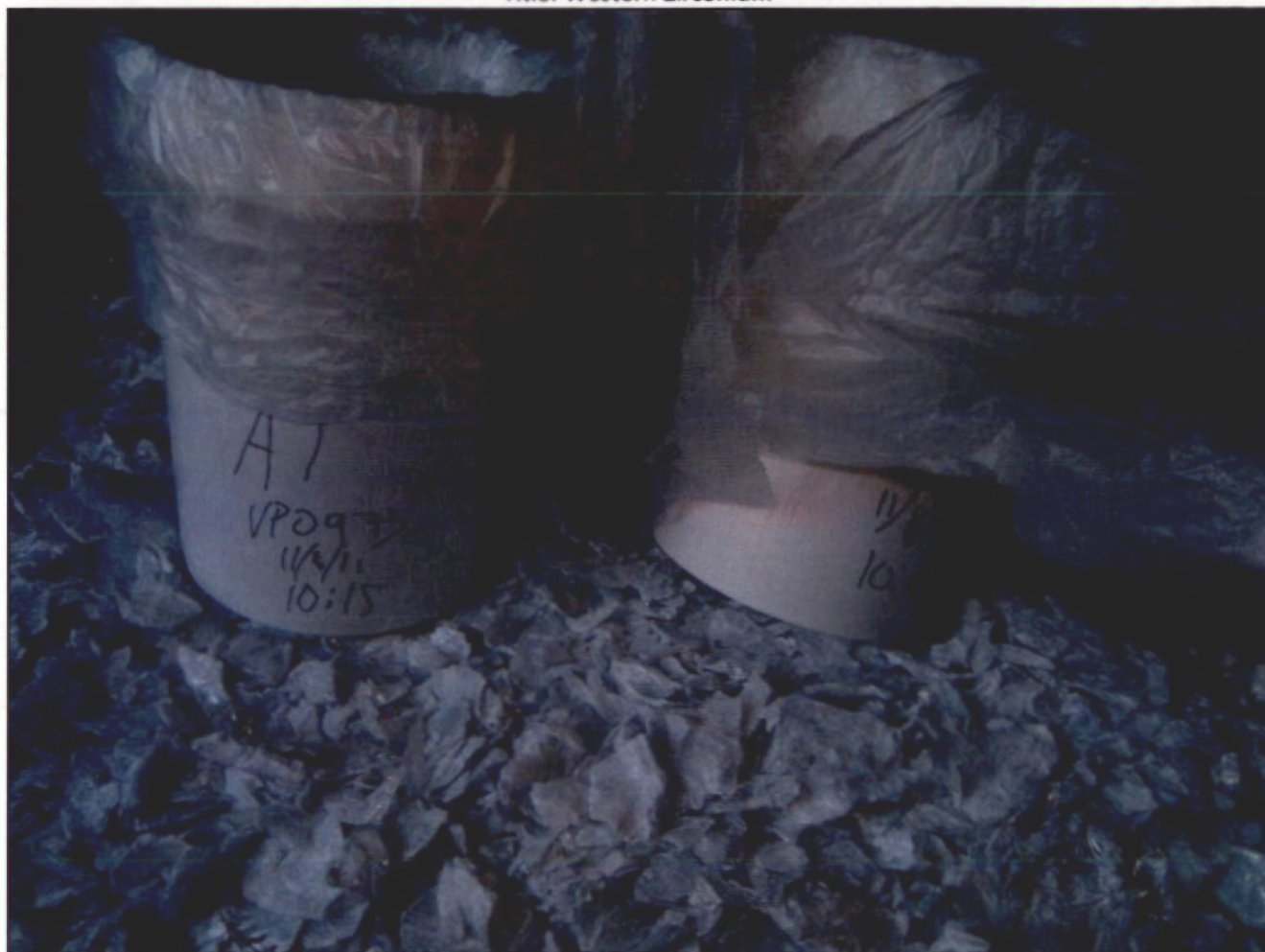
Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Magnesium chloride pile with sample A
Date Time Stamp	11/8/2011 10:42:29 AM
File Name	RIMG0010.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 49"
Photographer	Linda TeKrony

RIMG0011.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Label on sample A buckets
Date Time Stamp	11/8/2011 10:45:40 AM
File Name	RIMG0011.JPG
Latitude	N 41° 15' 44"
Longitude	W 112° 13' 49"
Photographers	Linda TeKrony

RIMG0012.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Label on sample A buckets
Date Time Stamp	11/8/2011 10:45:50 AM
File Name	RIMG0012.JPG
Latitude	N 41° 15' 44"
Longitude	W 112° 13' 49"
Photographer	Linda TeKrony

RIMG0013.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Bottom of silo to be sampled for Sample C
Date Time Stamp	11/8/2011 11:19:39 AM
File Name	RIMG0013.JPG
Latitude	N 41° 15' 44"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0014.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Sample B pile prior to splitting
Date Time Stamp	11/8/2011 11:22:53 AM
File Name	RIMG0014.JPG
Latitude	N 41° 15' 44"
Longitude	W 112° 13' 47"
Photographer	Linda TeKrony

RIMG0015.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Sample C inside of bucket after splitting with sample scoop
Date Time Stamp	11/8/2011 11:29:28 AM
File Name	RIMG0015.JPG
Latitude	N 41° 15' 44"
Longitude	W 112° 13' 47"
Photographer	Linda TeKrony

RIMG0016.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Sample C at sample location
Date Time Stamp	11/8/2011 11:32:54 AM
File Name	RIMG0016.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 47"
Photographer	Linda TeKrony

RIMG0017.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Label on sample C bucket
Date Time Stamp	11/8/2011 11:33:03 AM
File Name	RIMG0017.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 47"
Photographer	Linda TeKrony

RIMG0018.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Mist sample on chunks of magnesium chloride
Date Time Stamp	11/8/2011 11:45:43 AM
File Name	RIMG0018.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 49"
Photographer	Linda TeKrony

RIMG0019.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Spraying water on large chunk of magnesium chloride
Date Time Stamp	11/8/2011 11:46:21 AM
File Name	RIMG0019.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 49"
Photographer	Linda TeKrony

RIMG0020.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Additional chunk of magnesium chloride
Date Time Stamp	11/8/2011 11:47:33 AM
File Name	RIMG0020.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0021.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Spraying water on additional chunk of magnesium chloride
Date Time Stamp	11/8/2011 11:48:00 AM
File Name	RIMG0021.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 49"
Photographer	Linda TeKrony

RIMG0022.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Backhoe moving magnesium chloride to the hopper prior to the grinder
Date Time Stamp	11/8/2011 12:11:27 PM
File Name	RIMG0022.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0023.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Top of second crucible
Date Time Stamp	11/8/2011 12:19:13 PM
File Name	RIMG0023.JPG
Latitude	N 41° 15' 42"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0024.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Top of second crucible
Date Time Stamp	11/8/2011 12:19:22 PM
File Name	RIMG0024.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0025.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Pile of Grade B magnesium chloride
Date Time Stamp	11/8/2011 12:23:29 PM
File Name	RIMG0025.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0026.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Pile of Grade B magnesium chloride that was actually sampled
Date Time Stamp	11/8/2011 12:27:16 PM
File Name	RIMG0026.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0027.JPG
Title: Western Zirconium



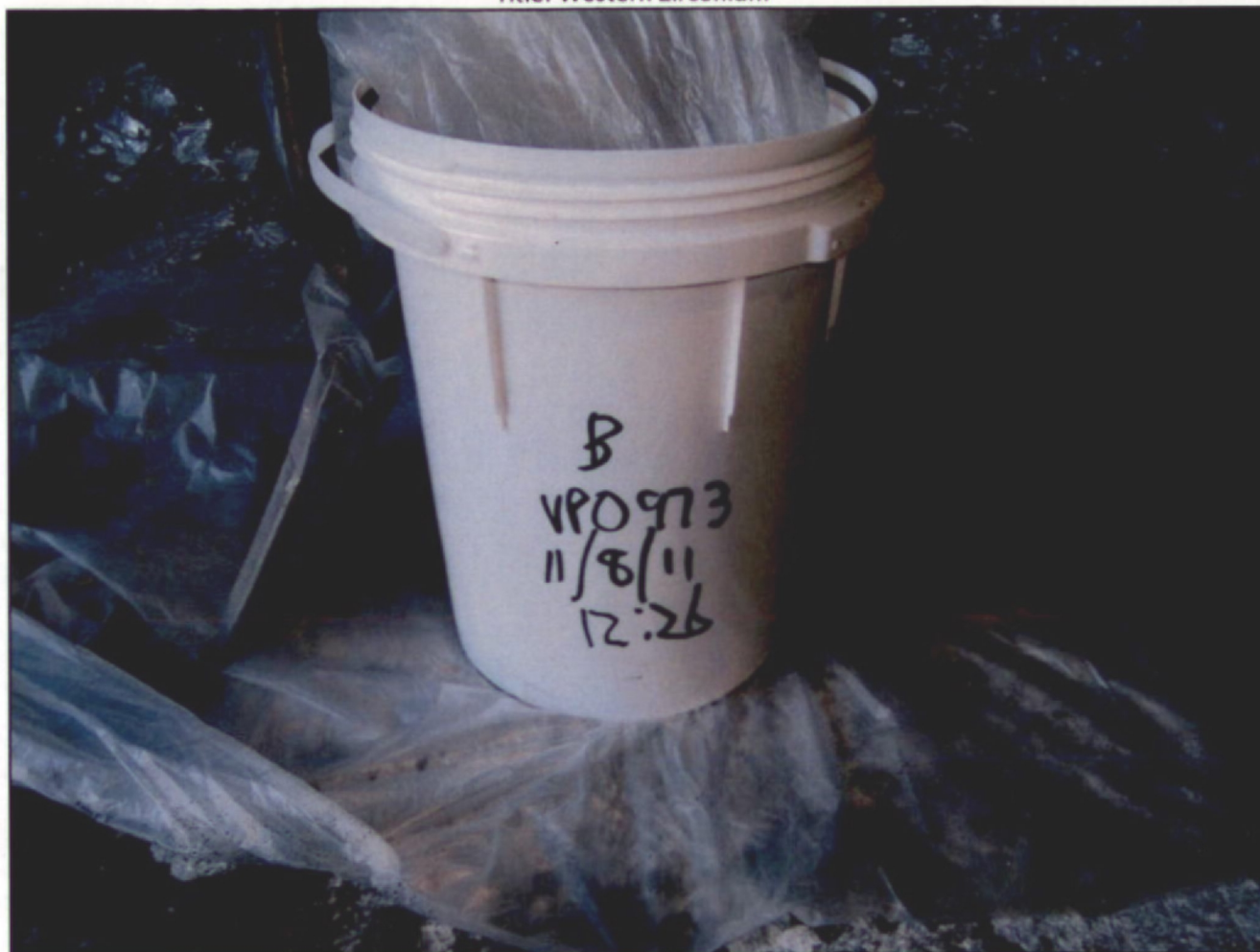
Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Two buckets of Sample B
Date Time Stamp	11/8/2011 12:36:10 PM
File Name	RIMG0027.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0028.JPG
Title: Western Zirconium



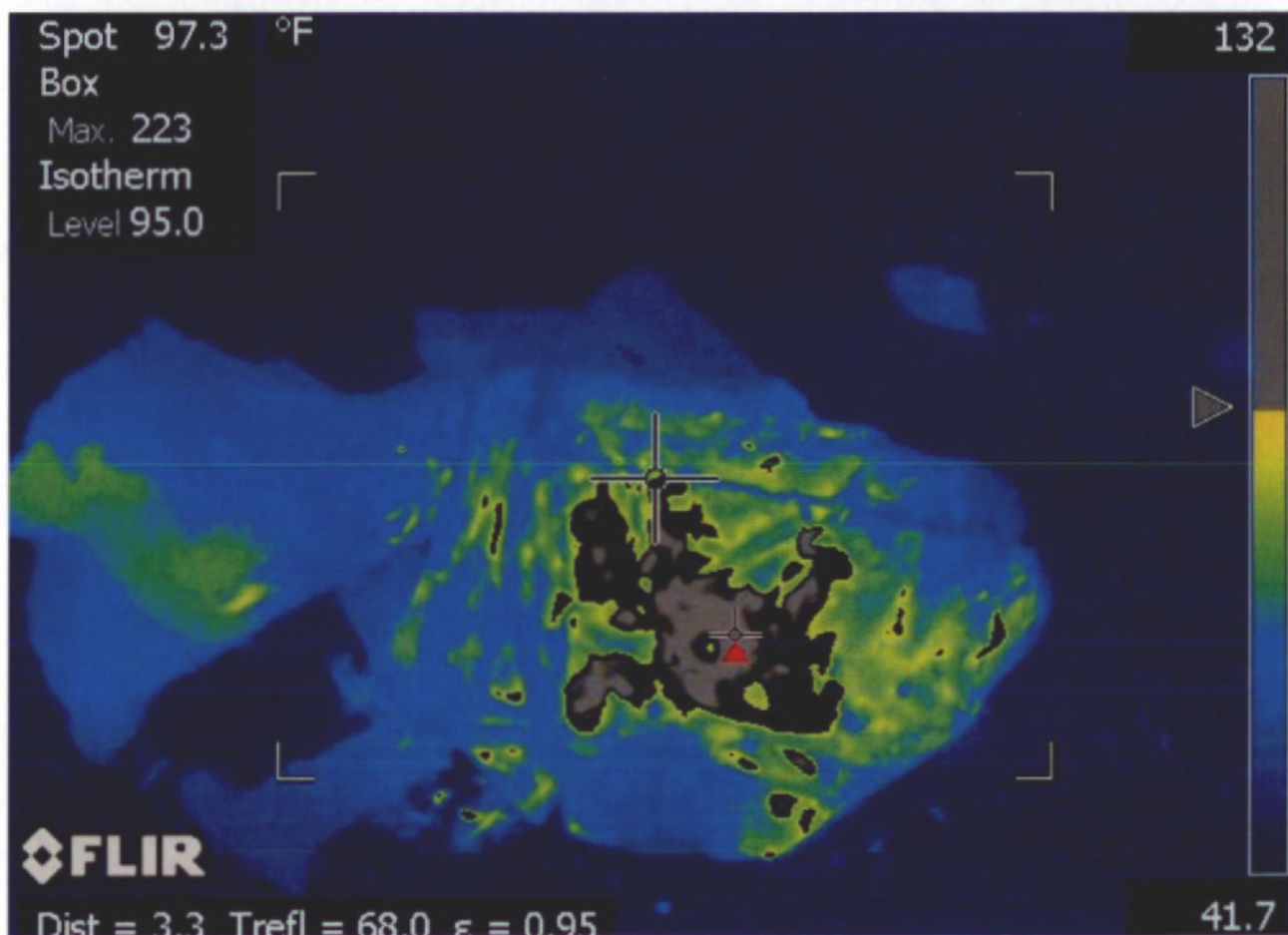
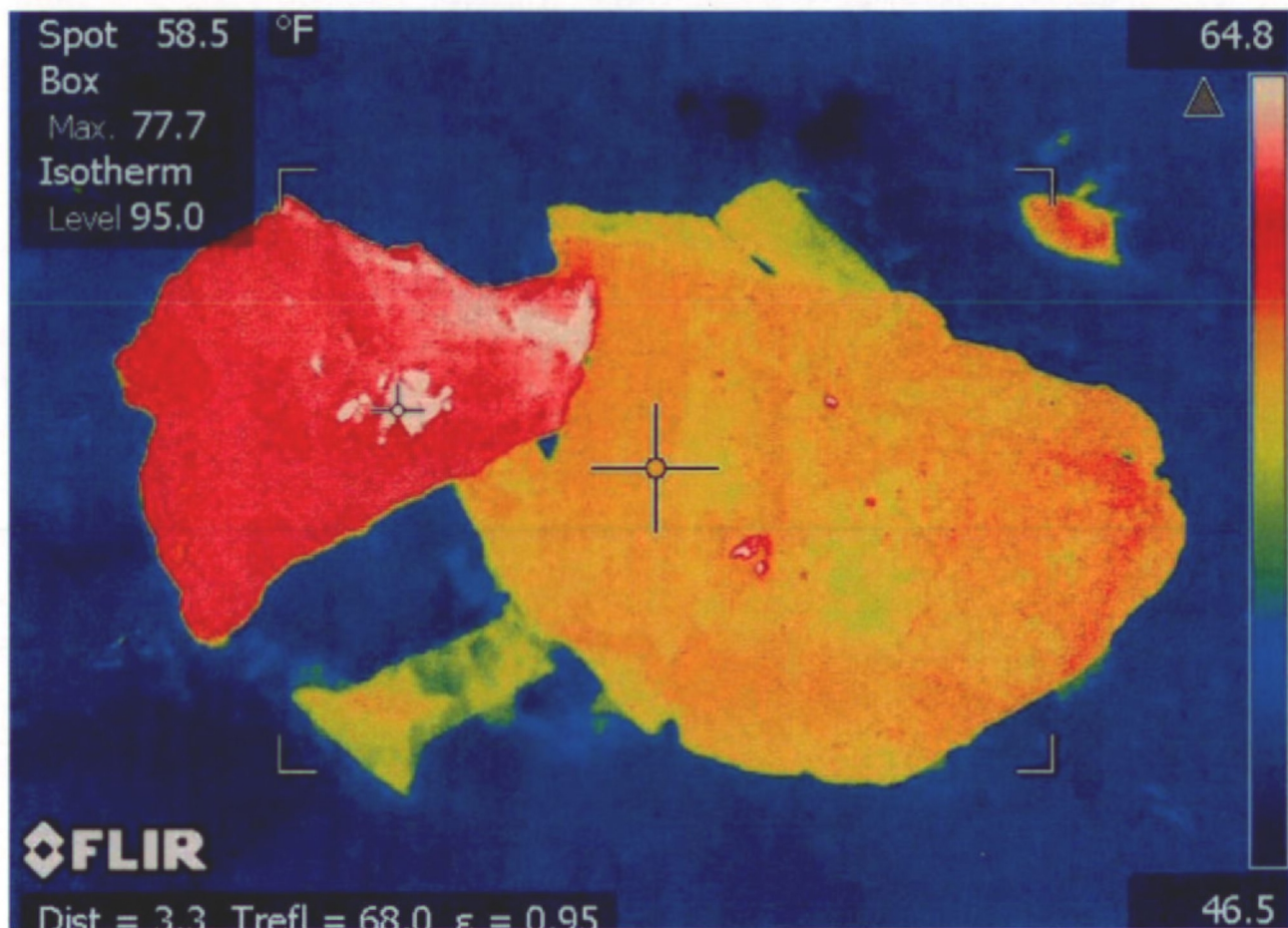
Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Sample container of Sample B
Date Time Stamp	11/8/2011 12:38:51 PM
File Name	RIMG0028.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

RIMG0029.JPG
Title: Western Zirconium



Attributes	
Title	Western Zirconium
Subject	VP0973
Description	Label on Sample B bucket
Date Time Stamp	11/8/2011 12:38:58 PM
File Name	RIMG0029.JPG
Latitude	N 41° 15' 43"
Longitude	W 112° 13' 48"
Photographer	Linda TeKrony

APPENDIX B
NEIC INFRARED PHOTOGRAPHS
(1 page)



APPENDIX C

NEIC CHAIN OF CUSTODY, RECEIPT FOR SAMPLES, AND TRANSFER OF SAMPLES
(3 pages)

NEICVP0973E01

Appendix C

Western Zirconium
Ogden, Utah

Distribution: Original Accompanies Shipment; Copy to Coordinator Field Office

RECEIPT FOR SAMPLES

[illegible]

Distribution: Original to Coordinator Field Files; Copy to Facility

N 61057

NATIONAL ENFORCEMENT INVESTIGATIONS CENTER
Building 53, Box 25227, Denver Federal Center
Denver, Colorado 80225

Transferred by (Signature) <i>[Signature]</i>		Received by (Signature) <i>[Signature]</i>		Telephone 801-732-2443
Date 11/08/2011	Time 13:10	Title Sr. Env. Engr.	Date 11-8-11	Time 13:10

N 15222

Western Zirconium
Ogden, Utah